

Research Laboratory
of the
Portland Cement Association

BULLETIN 10

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Phase Diagrams of
Ternary Systems

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INTERPRETATION OF PHASE DIAGRAMS OF TERNARY SYSTEMS

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Conventional interpretations of phase diagrams of systems of the refractory oxides describe the order of appearance and disappearance of solid phases when liquids of various compositions are cooled slowly. In applying phase equilibria data to problems pertaining to portland cement manufacture, in which raw material mixtures are only partially fused, it has been found advantageous to follow a somewhat different mode of attack. Methods have been developed for determining the phases present at equilibrium at any given temperature, and esti-

mating their proportions, without tracing the course of crystallization from the liquid state. In addition, attention has been given to the rôle of the liquid phase in the processes of fusion and crystallization, as a means of gaining an understanding of the mechanism by which the oxides in the raw materials are transformed into the various cement compounds. These methods may be found useful in other fields, and are consequently presented in this paper in a study of hypothetical ternary systems. The paper deals only with condensed systems in which the solid phases are practically immiscible.

IDEAL CONDITIONS OF CRYSTALLIZATION

In descriptions of the course of crystallization it is customary to assume an ideal condition, in which cooling is so slow that at each temperature a state of equilibrium is attained before a further reduction in temperature takes place. This condition may be described as a continuous attainment of equilibrium during the process of cooling. When there is a continuous attainment of equilibrium, the phase diagram supplies all of the information necessary to predict the phases present at any stage in the process, and to estimate their proportions, by a process of deduction involving the mathematical properties of the triangular diagram.

With a slow attainment of equilibrium the process of cooling must be extremely slow if a continuous attainment of equilibrium is to be secured. The conclusions in regard to the course of crystallization, obtained by assuming a continuous attainment of equilibrium, consequently apply only to cases in which the process of cooling is so slow that this condition is secured. In an industrial process the condition must be known to exist before it can be assumed that the predicted changes in character and proportions of phases actually occur. It is not enough to know that a time element is involved in the process. It must be known that the rate of temperature change in the process is *sufficiently* slow to secure the continuous attainment of equilibrium. This cannot be known from the phase diagram, but can only be known by observations in addition to those represented in the diagram.

The purpose of this paper is to present methods of interpreting the phase diagram with reference to industrial processes. It will consequently not be confined to a study of changes occurring with a continuous attainment of equilibrium, but will deal also with the changes which may occur if temperature change is too rapid to permit such a condition to exist. Because of the fact that most discussions of the course of crystallization assume the continuous attainment of equilibrium, it will be necessary to depart from conventional methods of presenting the subject, and to adopt an entirely new method of treatment.

CONSIDERATIONS IN A CONDENSED SYSTEM

A condensed system is one in which a great increase in pressure is required to produce a small change in the temperature required for a given state of equilibrium. Phase equilibria in such systems may be investigated in open vessels

at atmospheric pressure, and yet yield data practically identical with those which would be obtained if the mixtures employed in the investigation were subjected only to the pressure of their own vapor. Since large changes in pressure are required to produce only a small change in the temperature required for a given state of equilibrium, the interpretation of the phase diagram of a condensed system does not involve consideration of pressure as a variable. In stating conditions imposed upon a system, temperature only will be mentioned.

When the composition and temperature of a condensed system are given, the character and proportions of phases, that is, the phase composition at equilibrium, is defined, except at the temperature at an invariant point,¹ and may be estimated from the phase diagram. Although the complete phase composition includes the vapor phase, the amount of material involved in the vapor phase is so small that it may be ignored. The vapor phase will consequently be ignored in discussing phase compositions, or changes in phase composition resulting from decrease in temperature (the process of crystallization) or from increase in temperature (the process of fusion).

According to modern theories of liquid structure, molecules may be associated in large aggregates, some of them in a relatively orderly arrangement. However, phase equilibria relations in a condensed ternary system are compatible with the simple assumption that liquids in the system are composed entirely of unassociated molecules of various kinds. Since this assumption is sufficient for the purpose at hand and helps to simplify treatment of the subject, it is adopted in the study which follows.

HYPOTHETICAL SYSTEM INVOLVING THREE SOLID PHASES

Let us consider first a simple ternary system involving three solid phases, *A*, *B*, and *C*. All mixtures of *A*, *B*, and *C* may be represented in a triangular diagram in the customary manner. If mixtures of a variety of compositions, scattered over the entire diagram, are melted, and the temperature of complete fusion is determined in each case, the data obtained establish isotherms in the diagram, as shown in figure 1.² Passing from *A* to *B*, that is, beginning with *A* and considering successive additions of *B*, it is seen from the diagram that the temperature of complete fusion drops from 117° at *A* to 75° at *H*, and then increases to 126° at *B*. The point *H* represents a eutectic composition, with a lower temperature of complete fusion than either *A* or *B*. Similarly, *K* is a eutectic mixture of *A* and *C*, and *G* is a eutectic mixture of *B* and *C*. The point *E* represents a eutectic mixture of the three components *A*, *B*, and *C*, with a lower temperature of complete fusion than any other mixture in the system.

The 50° and 60° isotherms are not continuous curves, but change abruptly in direction, forming a closed figure. If isotherms are drawn to represent intermediate temperatures, similar abrupt changes in direction will appear. The

¹ It will be shown later that at an invariant point the phase composition at equilibrium is defined by composition and heat content, not by composition and temperature.

² Since figures 1-12 refer to hypothetical systems, no attempt has been made to indicate temperatures in a range which would be encountered in systems of refractory oxides. Low temperatures are indicated merely for convenience.

curves EK , EH , and EG are the loci of the points at which such changes in direction occur. These curves divide the triangle into three regions. When any mixture within the region $EKCG$ is maintained at its temperature of complete fusion, it is capable of existing in equilibrium with solid phase C . Above that temperature it is liquid. Just below that temperature, if no supercooling occurs, the solid phase C separates out from the liquid. It is the first crystalline phase to appear in the normal process of crystallization, and is called the primary phase for that region. Similarly, solid phase A is the primary phase for the region $AKEH$, and solid phase B is the primary phase for the region $HEGB$.

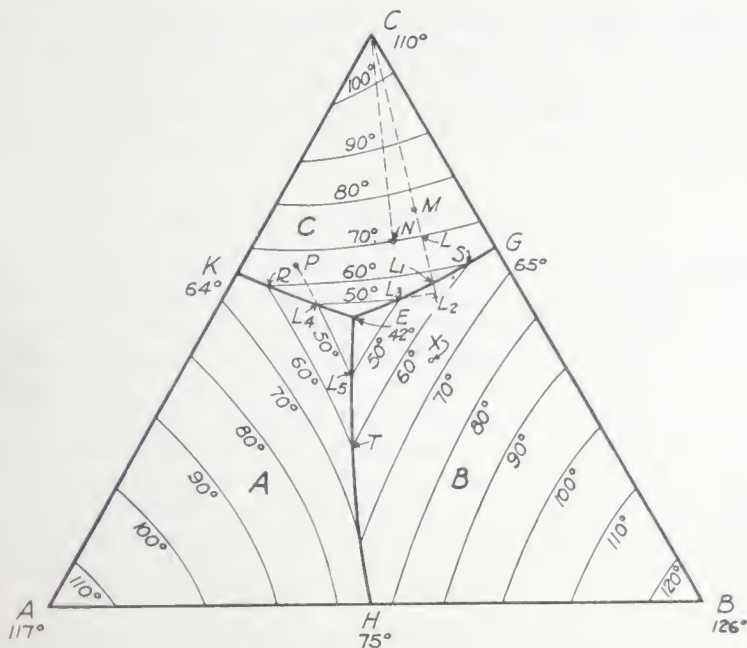


FIG. 1. Typical phase diagram of ternary system involving three molecular species.

The three regions are termed primary-phase regions. The letters A , B , and C in the three regions designate the primary phases.

When a system is in a state of equilibrium, the escaping tendency of each molecular species involved is constant throughout the system. Consider a liquid represented by a point on the line RS , which is the branch of the 60° isotherm in the C primary-phase region. When the liquid is in equilibrium with solid C at 60° , the escaping tendency of C from the liquid is equal to that of crystalline C . It is this balance between escaping tendencies which makes it possible for the two phases, solid C and liquid, to exist together without change. The term equilibrium implies a balance between forces or reactions, in this case escaping tendencies.

From the foregoing description of the conditions existing in a state of equilib-

rium, it is evident that at 60° the escaping tendency of the component C from all liquids on RS is the same. While the numerical value of this escaping tendency may not be known, it is known to be identical with that of solid C at 60° . The line RS consequently has a significance in addition to that of representing the locus of compositions with a temperature of complete fusion of 60° . It refers also to a particular solid phase, C , and may consequently be referred to as the $60^\circ C$ isotherm. All other isotherms in the C primary-phase region may thus be described as C isotherms. Similarly, all isotherms in the A primary-phase region are A isotherms, and all in the B primary-phase region are B isotherms.

The isotherms being considered with reference to temperatures of complete fusion, the figure RST may be regarded as a single isotherm, changing abruptly in direction at R , S , and T . From the standpoint of their significance with respect to escaping tendencies, the three branches must be regarded as separate isotherms, the $60^\circ A$ isotherm RT , the $60^\circ B$ isotherm ST , and the $60^\circ C$ isotherm RS .

Significance of the isotherm—supercooling

In ternary phase diagrams the separate isotherms meeting at the boundaries of two primary-phase regions are usually drawn only to those boundaries, giving the appearance of being single isotherms changing abruptly in direction. From the standpoint of their true significance, with reference to escaping tendencies, they may be considered as extending beyond the boundaries. For example, the $50^\circ A$ isotherm in figure 1 is extended by a broken line to the point P . If a liquid of composition P can be supercooled to 50° (through failure of solid C to appear), the escaping tendency of component A from the liquid will then be equal to that of pure solid A at that temperature. The liquid P will be capable of existing in equilibrium with solid A at 50° , and such a state of metastable equilibrium may be maintained indefinitely if solid C does not appear.

The point T , figure 1, is on both the A and B 60° isotherms. At 60° , then, the escaping tendency of component A from liquid T is equal to the escaping tendency of solid A at 60° , and the liquid may exist in equilibrium with solid A . Since it is also on the $60^\circ B$ isotherm, liquid T may exist in equilibrium with solid B . That is, as a result of the fact that T is on both the A and B isotherms for 60° , the liquid is capable of existing in equilibrium with two solid phases, A and B . From this it is seen that all liquids on EH may exist in equilibrium with two solid phases, A and B , or with either phase alone, at the indicated temperatures. Similarly, liquids on EK may exist in equilibrium with the solid phases A and C , and liquids on EG may exist in equilibrium with B and C , at the indicated temperatures.

The triangular phase diagram of a ternary system, such as that shown in figure 1, is the projection of a space model, in which the base is a triangular diagram and temperature is represented by distances in a direction perpendicular to the base. In this space model the primary-phase regions are curved surfaces meeting in "valleys" which, when projected on the base, are represented

by boundaries between primary-phase regions. A horizontal section through the space model at a distance from the base corresponding to a particular temperature will cut the curved surfaces along curved lines which are isotherms. The isotherms in the phase diagram are projections of these lines on the base. Viewing figure 1 in this manner we can see that in the space model there are three surfaces sloping down from the vertices to EK , EH , and EG , and that they intersect at E , the lowest point. The surface $AKEH$, representing conditions under which liquids may exist in equilibrium with solid A , may be termed the A surface. Similarly, the surface $HEGB$ is the B surface, and $EKCG$ the C surface.

Attention has been called to the fact that the isotherms in one region may be extended into another region, as shown in extending the $50^\circ A$ isotherm to P . This is equivalent to an extension of one surface beyond the curve of intersection with another surface (the curves EK , EH , and EG). In that case the A surface, extended, passes under the B and C surfaces, etc. Each surface shown in the diagram is the *upper* surface in the region indicated.

Other molecular species, that is, various combinations of A , B , and C , may be present in the liquid. However, since these molecular species are not represented by surfaces above those of A , B , and C , they may be ignored in considering solid-liquid equilibria. As A , B , and C are removed from the liquid in the process of crystallization, these other molecular species dissociate to release more A , B , and C . There is consequently no residue of other substances when crystallization is complete.

If the surfaces are considered as extending beyond the limits shown, it is evident that there will be a $40^\circ A$ isotherm below the B and C surfaces. If 42° isotherms are drawn for the three surfaces, they will intersect at E . Since a liquid of composition E at 42° is on the A , B , and C 42° isotherms, it is capable of existing in equilibrium with the three solid phases A , B , and C .

Tracing the course of crystallization

The phase diagram designates the phases which may exist in equilibrium in a heterogeneous system at a given temperature, but does not give directly any other information concerning the phases present, or their proportions, in the system. That is, one cannot locate in the phase diagram a point representing the composition of a particular system and then determine the phase composition by mere inspection. However, the phases which may exist in equilibrium are given in the diagram and only certain combinations of these phases are mathematically capable of forming any given composition. It is consequently possible to combine the information from the phase diagram with the mathematical possibilities concerning the combinations of phases which may form the composition of a mixture, and thus determine the phase composition. In this study an effort will be made to distinguish between the information obtained from the phase diagram and that obtained solely from mathematical considerations.

For our first problem, let us assume that a mixture of composition M (figure

1) is maintained at 70° . The problem is to determine the phase composition when equilibrium is attained. The position of M with reference to the isotherms indicates that its temperature of complete fusion is greater than 70° (about 75°). Hence it is known that the mixture M will be partly solid at 70° . Since the $70^\circ C$ isotherm is entirely within the C primary-phase region, in which M lies, it is known that the mixture M will be composed of solid C and liquid when in equilibrium at 70° . Only liquids on the $70^\circ C$ isotherm may exist in equilibrium with solid C at that temperature. From the phase diagram, then, it is known that the phases are solid C and a liquid which must be on the $70^\circ C$ isotherm. This is all that is known from the conditions of phase equilibria represented in the phase diagram. To determine the particular liquid on the $70^\circ C$ isotherm which will be present, a knowledge of the mathematical properties of the triangular diagram is required.

When two substances represented by points in a triangular diagram are mixed, all compositions which may be formed by adjusting their proportions are located on the straight line joining the points. For example, if N is mixed with C (figure 1), all of the possible compositions are on the line NC . Although N is on the $70^\circ C$ isotherm, and therefore fulfills the condition set by the requirement of equilibrium between solid C and liquid, it is known from mathematical considerations that it cannot be the liquid present in M when a state of equilibrium is attained at 70° , since M is not on the line NC . The only liquid which fulfills both the phase equilibrium requirement (that the liquid must be on the $70^\circ C$ isotherm) and the mathematical requirement (that the point M must be on the line joining the two phases) is the point L . It is consequently known that when equilibrium is attained at 70° the mixture M is composed of solid C and liquid L .

The phases have been determined, and it is now necessary to determine their proportions. If the length of the line LC is taken as unity, the segment ML (farthest from C) is the fractional proportion of solid C . Similarly, the segment CM (farthest from L) is the fractional proportion of liquid L . By measurement it is found that the fractional proportion of solid C is 0.13 (or 13 per cent); the fractional proportion of liquid L is 0.87 (or 87 per cent).

If the mixture M is cooled to 55° and maintained at that temperature until equilibrium is attained, the composition of the liquid phase must then be on the $55^\circ C$ isotherm, about halfway between the 50° and 60° isotherms, and also on an extension of the line CM , that is, at L_1 . The system is then composed of solid C and liquid L_1 . The effect of reducing the C content of the liquid, in this case by crystallization, is to change its composition in a direction away from the point C . This may be stated briefly, speaking with reference to the position of the liquid in the diagram, by saying that the removal of C from the liquid forces the liquid directly away from C .

Now if the mixture is cooled to 50° , with no other phenomenon but the separation of solid C , the liquid is forced to L_2 , on an extension of the $50^\circ C$ isotherm. However, the liquid is now in the B primary-phase region. If B separates out, the liquid is forced directly away from B , that is, toward a point on EG between L_1 and L_3 . The combined effect of the tendency to change in a

direction away from C , when in the C primary-phase region, and away from B , when in the B primary-phase region, is to cause the liquid composition to follow the boundary curve EG . If the solid phase B fails to appear, the liquid will have the composition L_2 when equilibrium is attained. It is then in a state of metastable equilibrium, since the state of equilibrium may be disturbed in various ways, causing the separation of B . If crystallization of B is sluggish, the composition of the liquid will follow a path in the B primary-phase region between the extended $50^\circ C$ isotherm and the boundary curve EG , finally arriving at L_3 when equilibrium is attained. If crystallization of B is rapid, the composition of the liquid will follow the boundary curve EG from L_1 to L_3 . When equilibrium is attained at 50° , the mixture M will be composed of solid B , solid C , and liquid L_3 .

If the mixture is now cooled to 42° the liquid will follow the boundary curve EG to E , with further separation of solid B and C . When the liquid arrives at E the mixture is composed of solid B , solid C , and liquid E . At this point the liquid is capable of existing in equilibrium with the three solid phases A , B , and C . Upon further removal of heat, solid A , B , and C separate out, until the last trace of liquid disappears. This occurs without change of temperature, since the heat which is withdrawn is the latent heat released in the process of crystallization. When crystallization has been completed at 42° , further removal of heat results in a decrease in temperature.

It was mentioned earlier that during the crystallization of mixture M the liquid is forced to follow the boundary curve EG by the crystallization of B . If solid B fails to separate out, the liquid will follow the extension of the line $M-L_1$ into the B primary-phase regions. A similar situation arises after the liquid arrives at E along the boundary curve EG . If C appears, the liquid remains at E until crystallization is complete. If solid C fails to appear, the liquid will follow an extension of the boundary curve EG into the A primary-phase region.

Determination of phase composition without tracing the course of crystallization

The phases present in the mixture M when a state of equilibrium is attained at 50° have been found by following the course of crystallization from higher temperatures, the customary procedure in studies of the course of crystallization. It must not be supposed, however, that the phases present at equilibrium can be determined only by starting with the fused mixture, and tracing the appearance and disappearance of solid phases as the mixture is cooled. The equilibrium state at 50° is the same whether the mixture is first fused and then cooled, or is heated from a lower temperature to 50° . This should be clearly understood, since in many cases as, for example, in the production of portland cement clinker, the original solid materials are only partially fused. In studying such processes it is convenient to be able to determine the phases present without tracing the course of crystallization from complete fusion to the required temperature. On that account the phases present in the mixture M at equilibrium at 50° will be determined again, this time without tracing the path followed by the liquid composition (the crystallization curve) from M to L_1 , and then to L_3 .

First of all, it is known that the mixture is not composed of only two phases,

solid and liquid, since no point on the $50^\circ C$ isotherm is in line with C and M . If three phases are present they must be the phases designated at a 50° point on a boundary curve, such as L_3 , L_4 , or L_5 . Any mixture composed of three phases must be within the triangle formed by joining the points representing the compositions of the phases by straight lines. For example, since L_4 is on the boundary between the A and C primary-phase regions, the only mixtures in which L_4 may be present at equilibrium at 50° are those within the triangle formed by drawing straight lines from A to C , from C to L_4 , and from L_4 to A . By mere inspection it is seen that M does not lie in the triangle, and it is known, therefore, that the liquid L_4 is not present in M under the required conditions. Similarly, if L_3 is the liquid phase the point M must be within the triangle formed by joining L_3 , B , and C by straight lines, which it is. These three phases, solid B , solid C , and liquid L_3 , are therefore the phases present.

With a simple phase diagram, such as figure 1, and with experience in tracing the course of crystallization, one would naturally test L_3 first as the possible liquid phase, with no need of inspecting a number of such points before finding L_3 to be the liquid phase. However, without such experience, or in more complicated situations, the method just described may be used. It has been given merely to demonstrate the fact that the phases present at equilibrium may be determined without tracing the course of crystallization.

The phases in M at equilibrium at 50° have been determined by two methods, but their proportions have not been estimated. In discussions of the course of crystallization it is customary to estimate the relative proportions of liquid and solid, and then to estimate the relative proportions of the two solid phases in the solid portion. This is not entirely satisfactory, since it is possible for a solid phase to decrease in amount and yet form an increasing proportion of the total solids, or *vice versa*. By following this procedure, the direction of change in the amount of a particular solid phase during crystallization or fusion can be determined, but only in an indirect fashion. In this study a direct method will be employed, in which the proportions of the liquid and the two solid phases are estimated simultaneously.

The points representing the mixture M and the liquid phase L_3 have been transferred from figure 1 to figure 2. The triangle $B-L_3-C$ includes the composition of all mixtures which are composed of solid B , solid C , and liquid L_3 at equilibrium at 50° . Broken lines are drawn from M , parallel to two sides, dividing the third side into segments proportional to the amounts of the three phases. If the length of BC is taken as unity, the segment VW is the fractional proportion of liquid L_3 (at the vertex opposite BC), the segment CV (farthest from B) is the fractional proportion of B , and the segment BW (farthest from C) is the fractional proportion of C , in the mixture M . Any side of the triangle may be subdivided by this procedure for estimating phase composition.

The examples given have illustrated methods of determining phase composition when the liquid phase is located in a primary-phase region or on a boundary between primary-phase regions. In each case the phase composition of a system in a state of equilibrium is completely determined by the composition and tem-

followed by the liquid phase during slow cooling of certain mixtures originally in a state of equilibrium above 42° , as was illustrated by a study of the mixture M . When such a mixture is slowly cooled to 42° , so slowly that a practically continuous state of equilibrium is attained, it will consist of solid B , solid C , and liquid E . The compositions which may attain such a state of equilibrium at 42° are included in the triangle formed by joining the points B , C , and E by straight lines, as shown in figure 3, to which the point E in figure 1 has been transferred. This triangle therefore represents system I. Similarly, system II is represented by triangle ACE , and system III by triangle ABE , in figure 3.

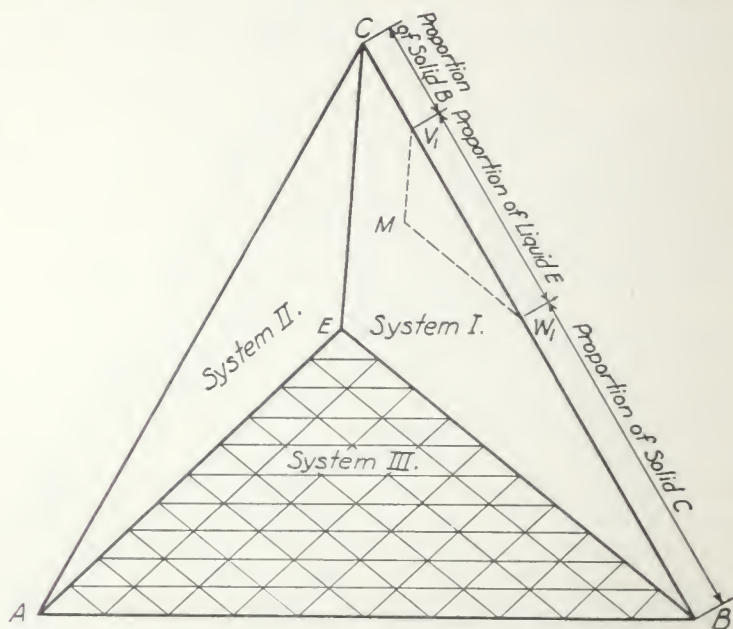


FIG. 3. Systems with two solid phases and a eutectic liquid E . Maximum heat content at eutectic temperature (also maximum proportion of liquid at eutectic temperature).

It will be observed that each triangle in figure 3 represents a system composed of three phases, one of them liquid, at equilibrium at 42° . The phase composition of any mixture under these conditions may be determined. For example, the proportions of solid B , liquid E , and solid C in the mixture M , which is the same as M in figures 1 and 2, are indicated by the segments CV_1 , V_1W_1 , and W_1B , respectively. Phase compositions may also be represented by drawing lines parallel to the three sides, as in system III, figure 3, in the same manner as is customary for the equilateral triangular diagram.

Systems of maximum and minimum heat content

When heat is withdrawn from any mixture in the state of equilibrium represented by the three systems in figure 3, a fourth phase appears, if there is no

supercooling. That is, liquid *E* and solids *A*, *B*, and *C* are then present. As heat is withdrawn the amount of liquid decreases without change of temperature, until finally only solid *A*, solid *B*, and solid *C* are present. The systems I, II, and III are therefore systems of maximum heat content at 42° , and refer to the state of equilibrium at 42° in which a maximum of liquid *E* is present. System IV, which represents the state of equilibrium at 42° when sufficient heat is removed to cause all liquid to disappear, is the system of minimum heat content at 42° . Since the phases then are the solids *A*, *B*, and *C*, the entire triangle *ABC* is required to represent system IV, as shown in figure 4.

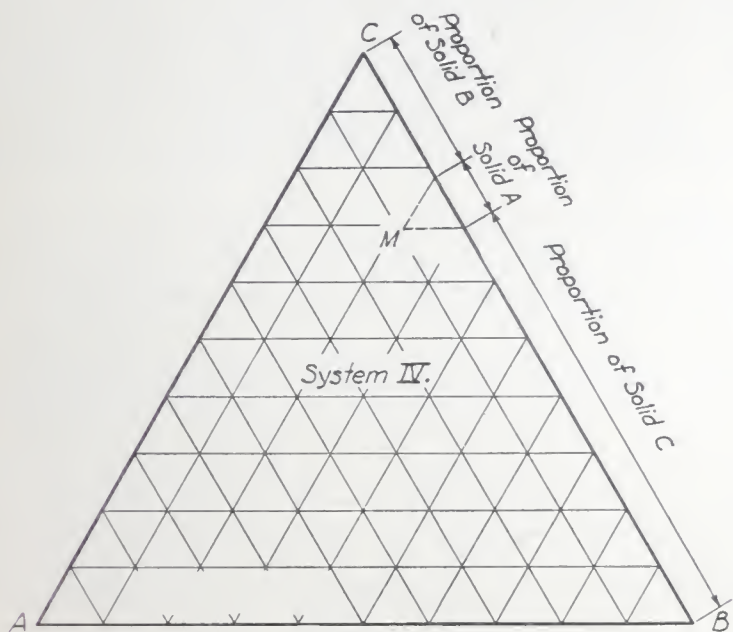


FIG. 4. System with three solid phases at eutectic temperature. (Final products of crystallization.) Minimum heat content at eutectic temperature.

The phase composition when crystallization is completed at 42° may be estimated by either method described in connection with figure 3. Both methods are represented in figure 4.

In showing only a portion of the phase diagram it is sometimes convenient to designate the 10 per cent intervals along the sides of the diagram, as shown along part of the base *AB* in figure 4. These points are represented by short segments of the longer lines in the figure, drawn parallel to the sides of the triangle.

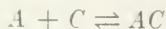
From the foregoing study it should be clear that the states of equilibrium represented by an invariant point include a range of possible phase compositions, from maximum to minimum heat content, at a single temperature. Between the maximum and minimum heat content four phases are present. The phase

composition at equilibrium is consequently defined not by composition and temperature but by composition and heat content.

For condensed systems it may be stated in general that the phase composition of a system is defined by composition and heat content. The phase composition is defined by composition and temperature in all cases in which change in heat content is accompanied by a change in temperature. These latter cases include all states of equilibrium represented in the phase diagram except those in which the liquid is at an invariant point.

In setting up the diagram in figure 1 it was assumed that only three solid phases were involved in the crystallization of liquids composed of the components *A*, *B*, and *C*. It was recognized that other molecular species, that is, various combinations of *A*, *B*, and *C*, might be present in the liquid, but these do not appear as solid phases. It will now be assumed that one of these molecular species, the compound *AC*, appears in the crystallization of liquids composed of *A*, *B*, and *C*. The surface representing the relation of escaping tendencies of *AC* in the liquid to that of solid *AC* must then be the upper surface in some region in the phase diagram.

If there were no reactions in which *A* and *C* combine to form *AC*, and *AC* dissociates into *A* and *C*, the system *A-B-C-AC* would have to be treated as a quaternary system, requiring a space model to represent phase equilibria relations. On the other hand, since such reactions do occur in the liquid phase, the system *A-B-C* is a ternary system, with a solid phase *AC* as one of the products of crystallization. Any state of equilibrium involves a state of homogeneous equilibrium in the liquid phase and a state of heterogeneous equilibrium with reference to the phases present. Under these conditions the disturbance of the equilibrium state in the liquid caused by the removal of *A*, *C*, or *AC* in the process of crystallization results in reactions within the liquid in a direction which will supply more molecules of the substance separating out. These reactions may be successive reactions involving molecular species other than those which have been considered. The net result, however, may be represented by the reversible reaction,



which proceeds toward the right if *AC* is removed from the liquid, and to the left if *A* or *C* is removed. For the purpose of this study it is possible to ignore the presence of molecular species other than those represented by primary-phase regions, and to refer to the liquid as being composed of *A*, *B*, *C*, and *AC*.

Introduction of AC equilibrium surface

It will be assumed that the *A*, *B*, and *C* surfaces in figure 1 also exist in the system now under consideration in which *AC* is a product of crystallization. These surfaces have been transferred to figure 5, and *AC* isotherms added to represent contours of the *AC* surface. Dotted lines in these figures represent loci of intersections of the *AC* isotherms with corresponding isotherms on the *A*, *B*, and *C* surfaces. These lines bound a region *K*₁-*E*₂-*E*₁-*K*₂ in which the *AC* surface is above the *A*, *B*, and *C* surfaces. This is the primary-phase region for *AC*, as shown in figure 6.

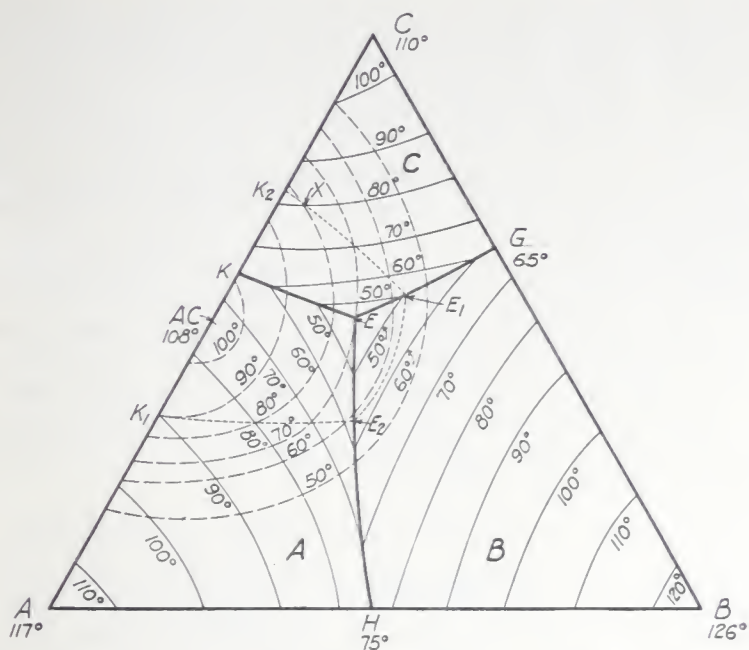


FIG. 5. Diagram illustrating effect of adding a fourth molecular species to system originally assumed to involve three molecular species.

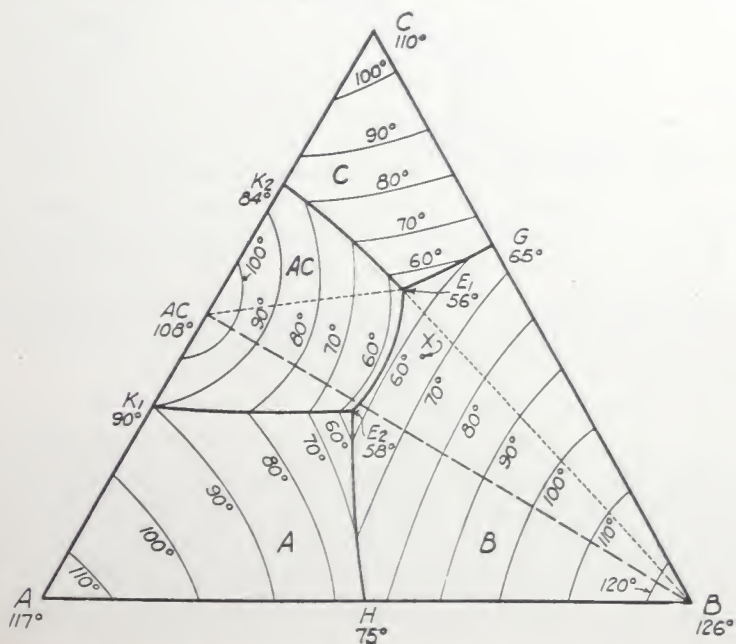


FIG. 6. Phase diagram resulting from hypothesis assumed in figure 5

The A , B , and AC surfaces slope downward toward the point E_2 , where they intersect. The point E_2 is therefore the eutectic for these three solid phases. A liquid of composition E_2 may exist in equilibrium with solid A , B , and AC at the temperature indicated (about 58°). Similarly, E_1 is the eutectic for the three solid phases B , C , and AC . The eutectic E for the solid phases A , B , and C (figure 1) does not appear, but is still present below the AC surface. It is significant under the present assumption only in case of supercooling in which the solid phase AC fails to appear.

Since solids B , C , and AC may exist in equilibrium with liquid E_1 at 56° , it is known that any two or any three of these phases may exist in equilibrium at 56° . Thus it is known that the three solid phases B , C , and AC may exist in equilibrium. The triangle B - C - AC includes all possible mixtures of the three solid phases. The solid phases at the vertices are the solid phases present when compositions within the triangle are completely crystallized. Similarly, the solid phases at the vertices of the triangle A - B - AC are the final products of crystallization of all compositions within this triangle.

Construction of triangles representing final products of crystallization

The broken line AC - B divides the diagram into two triangles, each representing final products of crystallization of all compositions within the triangle. In the interpretation of phase diagrams of this type, the lines dividing the phase diagram into triangles representing final products of crystallization are required. A simple method may be given for determining which solid phases are to be joined by straight lines for that purpose.³ For each pair of solid phases which appear as primary phases in adjacent regions a straight line is drawn between the points representing their respective compositions. For example, the AC and B primary-phase regions are adjacent. A straight line is therefore drawn from AC to B . Similarly, since the A and AC primary-phase regions adjoin, a line must be drawn from A to AC . This line is already drawn, since it is a segment of the side A - C . In figure 6 there is only one line, AC - B , which needs to be added.

Instead of merely presenting figure 6 as a type of ternary phase diagram which might be encountered, it has been constructed on the assumption that AC is one of the molecular species in liquids in the system A - B - C , with its equilibrium surface above those of A , B , and C in a particular region. This mode of treatment has been adopted to form a basis for considering the rôle of the liquid phase during fusion and crystallization of mixtures in the system.

Chemical reactions during fusion and crystallization

In figure 6 four molecular species A , B , C , and AC are involved. The proportions of solid phases and liquid at a eutectic temperature may be found in the same manner as in the foregoing study of figure 1. Let us suppose that X is a mixture of the solid phases A , B , and C . Upon raising the temperature to 56° a liquid of composition E_1 will form. When liquid E_1 is in a state of homogeneous equilib-

³ This method may be applied to any condensed system in which the solid phases are practically immiscible.

rium at 56° , it contains definite proportions of A , B , C , and AC . Since it is formed at first from A , B , and C only, it can only attain this state by the reaction, $A + C \rightarrow AC$, the direction of the reaction being determined by the lack of AC . Since E_1 is above the A surface, A must tend to go into solution. As A , B , and C dissolve, the tendency is to form a liquid in which the proportions of A and C are such as to force the reaction $A + C \rightleftharpoons AC$ to the right. When sufficient AC is formed to cause the liquid to be incapable of existing in equilibrium with solid AC , then solid AC separates out, thus also assisting in forcing the reaction to the right. The tendency, then, is to dissolve solid A and C and form solid AC . From the fact that X is in the triangle AC - E_1 - B it is known that this process

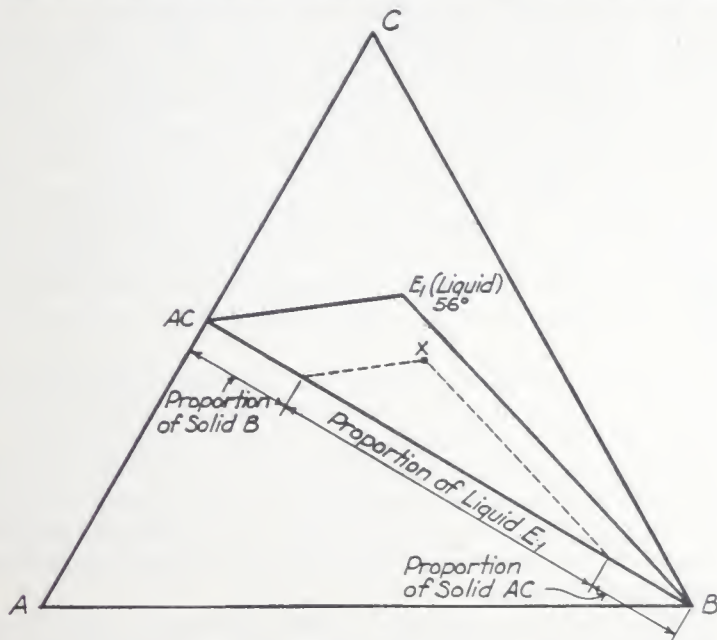


FIG. 7. Estimation of phase composition of mixture X (in figure 6) at equilibrium with maximum heat content at 56° .

continues until no solid A and C remain. When equilibrium is attained at 56° with maximum liquid (maximum heat content at 56°) the mixture X is composed of solid AC , solid B , and liquid E_1 , the latter, however, being composed of the four molecular species A , B , C , and AC . The proportions of the three phases may be determined graphically, as shown in figure 7.

Starting with composition X in a state of equilibrium at 56° with a maximum of liquid E_1 present, let us now consider the changes occurring as heat is withdrawn from the system. Since E_1 is at the intersections of the AC , B , and C primary-phase regions, it is known that solid AC , B , and C will separate out from the liquid as heat is withdrawn, if no supercooling occurs, but that any A which is present in the liquid will remain in solution. As AC , B , and C separate

out, the tendency is to increase the concentration of A in the liquid. The increase in concentration of A caused by the removal of the other three constituents of the liquid cannot progress far, since any increase in A forces the reaction $A + C \rightleftharpoons AC$ (in the liquid) to the right. As crystallization proceeds, this reaction in the liquid continues until, when the last drop of liquid disappears, no A remains. The mixture then consists of solid AC , B , and C .

Let us consider again the mixture X when equilibrium is attained at 56° with a maximum of liquid E_1 present. It is then composed of solid AC , solid B , and liquid E_1 . If the composition of X is to be expressed in terms of compounds present, rather than phases, percentages of at least four compounds would have to be given, since the liquid E_1 contains the four molecular species A , B , C , and AC .⁴ For some purposes the composition of X under the condition described may be expressed in terms of A , B , and C (the components of the entire system) or it may be expressed in terms of AC , B , and C (the final products of crystallization). Although in the latter case composition is expressed in terms of compounds, it does not represent the actual compound composition of the mixture, but merely a mathematical transformation of composition from one system of components to another. It is only when crystallization is complete that the actual compound composition, or chemical constitution of the mixture, is defined by expressing composition in terms of percentages of AC , B , and C , since it is only then that the composition expressed in these terms defines the phases and their proportions.

From the example just given it is evident that the process of crystallization in a system of the type shown in figure 6, in which there are more primary-phase regions than the number of components, is not a purely physical process. Each state of equilibrium represented is a state of balance between escaping tendencies of molecular species in the separate phases, as in the simple system considered in figure 1. In addition, however, there is a state of homogeneous equilibrium in the liquid phase, so that the process of crystallization and the reverse process of fusion involve chemical change.

The original mixture X was composed of solid A , B , and C . Upon being partially fused and again crystallized, it is composed of the solid phases AC , B , and C , not the original solid phases. In this process chemical reactions in the liquid phase play a prominent part, as has been shown. It is this function of the liquid phase which makes it possible, and also useful, to consider the individual systems A - B - AC and B - C - AC as being parts of a more complete ternary system, the system A - B - C .

SYSTEM INVOLVING INVARIANT POINTS WHICH ARE NOT EUTECTICS

Figure 8 is identical with figure 6, but isotherms representing contours of an A_nC surface have been drawn with broken lines, this surface representing the conditions under which a solid phase A_nC may exist in equilibrium with liquids in the system. It is assumed that there are reversible reactions involving

⁴ It is assumed in this statement that the components A , B , and C are compounds.

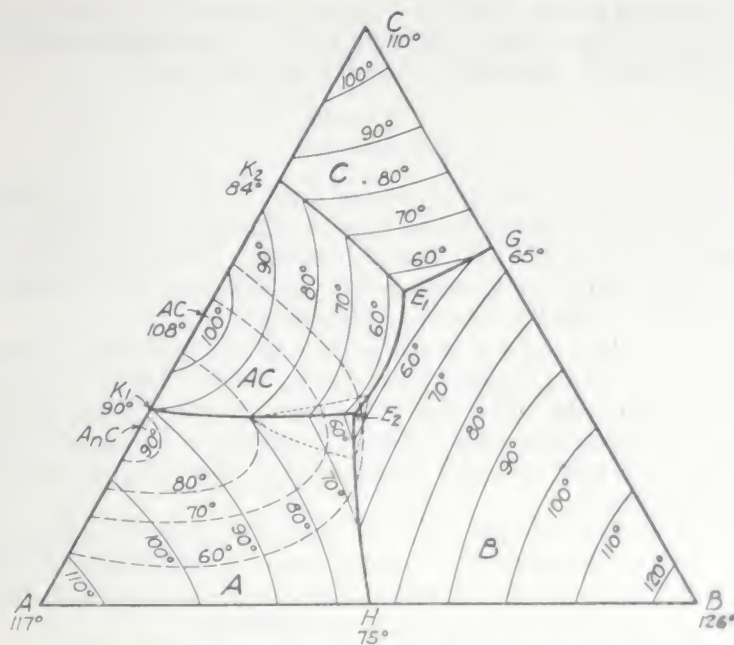


FIG. 8. Effect of adding a fifth molecular species to system assumed (in figure 6) to involve four molecular species.

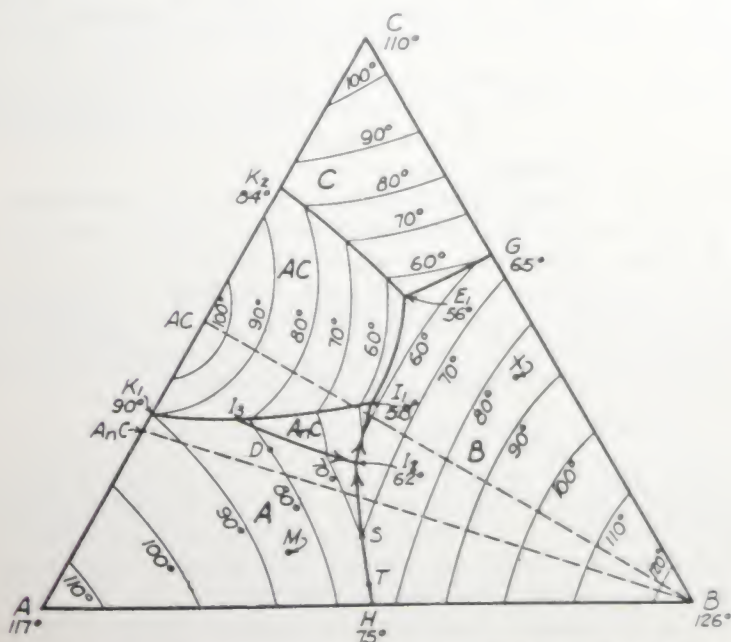
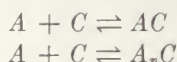


FIG. 9. Phase diagram resulting from hypothesis assumed in figure 8

the four molecular species A , AC , A_nC , and C , causing their concentrations to tend to change in such a way as to attain a state of homogeneous equilibrium. These reactions may be expressed in various ways, for example:



However these reactions may be expressed, there is for each composition and temperature a definite state of homogeneous equilibrium in the liquid, in which the concentrations of A , B , C , AC , and A_nC are fixed. The surfaces represent the conditions under which any liquid in a state of homogeneous equilibrium may exist in equilibrium with the respective solid phases.

The points at which the A_nC isotherms meet the corresponding isotherms in other regions are joined by dotted lines, forming a closed figure. In the region defined by this figure the A_nC surface is the upper surface. The region is therefore the A_nC primary-phase region. The A_nC isotherms in the region may therefore be drawn with solid lines, and those extending below other surfaces may be omitted, as in figure 9.

Since the primary-phase regions for A_nC and B are adjacent, a line is drawn between the points representing the compositions of the solid phases A_nC and B . Similarly a line is drawn from AC to B . The triangle ABC is thus divided into triangles representing the final products of crystallization.

When any mixture in the triangle AC - B - C is cooled slowly to permit the continuous attainment of equilibrium, a state of equilibrium is finally attained, at 56° , in which the liquid E_1 and the solid phases AC , B , and C are present. As crystallization proceeds the amounts of the three solid phases increase, until when crystallization is completed only the three solid phases are present. This may be described briefly by stating that all mixtures in the triangle AC - B - C complete their crystallization at E_1 . In such a statement it is not meant that the composition of the mixture is then E_1 , but that E_1 is the composition of the liquid at the last stage of the crystallization process.

Any mixture in a triangle representing final products of crystallization completes its crystallization at the point at which the three phases at its vertices may exist in equilibrium with liquid. Mixtures in the triangle A_nC - B - AC therefore complete their crystallization at I_1 . The point I_1 is outside of the triangle. It is consequently not classed as a eutectic, but as an "invariant point not a eutectic". Similarly, all mixtures in the triangle A - A_nC - B complete their crystallization at I_2 , which is also an invariant point, but not a eutectic.

Comparison of eutectic and non-eutectic invariant points

In the phase diagram of the type shown in figure 1 all mixtures in the triangle A - B - C complete their crystallization at 42° , with a liquid phase E present until crystallization is complete. The liquid E is a eutectic, since it is within the triangle. The direction of falling temperatures along the boundaries between primary-phase regions is toward the eutectic point, that is, from G to E , H to E , and K to E . At the eutectic temperature there are three systems of three phases

each, of maximum heat content, shown in figure 3, and one system of minimum heat content, shown in figure 4, the latter involving only solid phases, the final products of crystallization. Each of the triangles in figure 6, $A-B-AC$ and $AC-B-C$, may be given similar treatment.

At an invariant point which is not a eutectic the direction of falling temperatures is not toward the invariant point on all three of the boundaries meeting at the point. As a result, some compositions complete their crystallization at the invariant point, while others do not. Three invariant points which are not eutectics appear in figure 9. At I_1 and I_2 the direction of falling temperatures is away from the invariant point on one boundary. At I_3 the direction of falling temperatures is away from the point on two boundaries.

Crystallization after the liquid arrives at a non-eutectic invariant point may be illustrated in the case of I_2 . Mixtures in the triangle $A-A_nC-B$ complete their crystallization with the liquid at I_2 . On the other hand, when some mixtures in the triangle $A_nC-AC-B$ are cooled, the liquid arrives at I_2 at 62° and remains at that point, without change of temperature, until all of the solid A which may be present has disappeared. The liquid then follows the boundary I_2-I_1 to I_1 , where crystallization is completed.

Systems of maximum and minimum heat content

From figure 9 it is learned that at 62° the liquid I_2 may exist in equilibrium with the three solid phases A , A_nC , and B . All mixtures of the four phases must lie in the quadrilateral formed by joining points representing the compositions of the phases, that is, the quadrilateral $A-A_nC-I_2-B$ (figure 10). No mixtures outside of this quadrilateral can be composed of the four phases,—liquid I_2 and solids A , A_nC , and B .

Any three of the four phases may exist in equilibrium at 62° , giving the following systems of three phases:

- I. Solid A , solid A_nC , and liquid I_2
- II. Solid A , solid B , and liquid I_2
- III. Solid A_nC , solid B , and liquid I_2
- IV. Solid A , solid A_nC , and solid B

The diagonal $A-I_2$ divides the quadrilateral into two triangles, $A-A_nC-I_2$ and $A-B-I_2$, designated as system I and system II, respectively, in figure 10. These are systems of maximum heat content at 62° , as may be known from the fact that the solid phases represented at their vertices are primary phases in regions separated by a boundary on which the direction of falling temperature is toward I_2 . For example, in system I the solid phases are A and A_nC . The A and A_nC primary-phase regions, figure 9, are separated by the boundary curve I_3-I_2 , on which the temperature decreases as I_2 is approached. Systems I and II are also systems of maximum liquid content at 62° .

The diagonal A_nC-B divides the quadrilateral $A-A_nC-I_2-B$ into two triangles, A_nC-B-I_2 and $A-A_nC-B$, designated as systems III and IV, respectively, in figure 11. These are systems of minimum heat content. Mixtures in system III are

composed of liquid I_2 , solid A_nC , and solid B when equilibrium is attained at 62° , with minimum heat content. That is, they are not crystallized completely at 62° . Upon cooling below 62° , with a continuous attainment of equilibrium, the liquid phase changes in composition along the boundary curve I_2-I_1 , the direction of falling temperatures being away from I_2 toward I_1 .

Any mixture in the quadrilateral $A-A_nC-I_2-B$ is in either system I or system II, figure 10, with maximum heat content at 62° , and is in either system III or system IV, figure 11, with minimum heat content at 62° . For example, a mixture of composition M (figures 9, 10, and 11) is in system II, figure 10, when it is

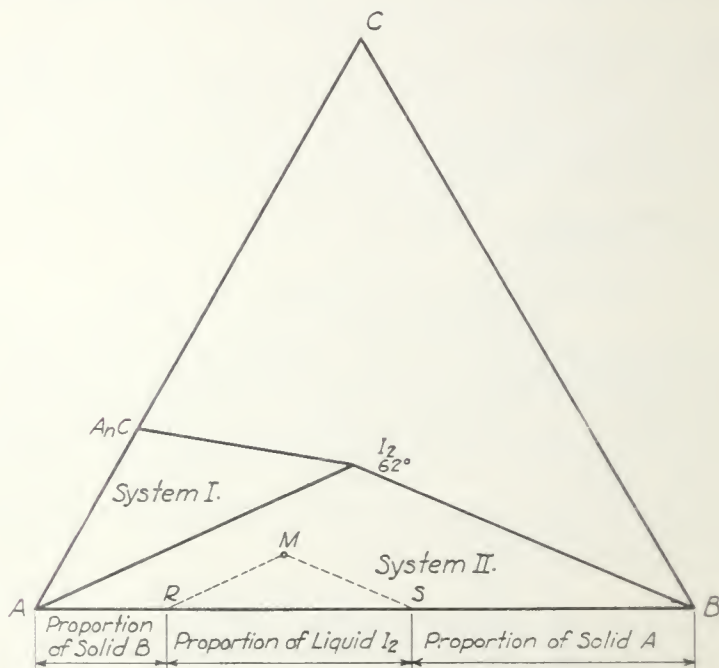


FIG. 10. Systems of maximum heat content at temperature at invariant point (also maximum proportion of liquid at that temperature).

at maximum heat content at 62° , and is composed of solid phases A and B and a maximum of liquid I_2 . When it is at minimum heat content at 62° it is in system IV, figure 11, and is composed of the three solid phases A , A_nC , and B .

The phase composition of mixture M at maximum and minimum heat content is estimated in figure 10 and 11, respectively. It can be seen by comparing the two figures that the proportion of solid A decreases in passing from maximum to minimum heat content. That is, there is more solid A present with a maximum amount of liquid I_2 than when crystallization is complete.

The decrease in quantity of solid A during crystallization at invariant point I_2 is of particular interest. The lines required in figures 10 and 11 for estimating

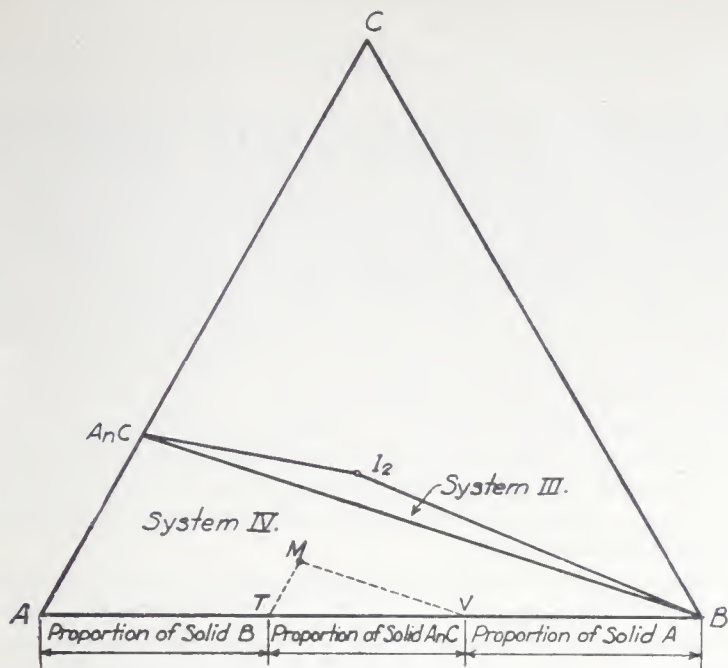


FIG. 11. Systems of minimum heat content at temperature at invariant point. (Minimum of liquid I_2 in system III, and complete crystallization in system IV.)

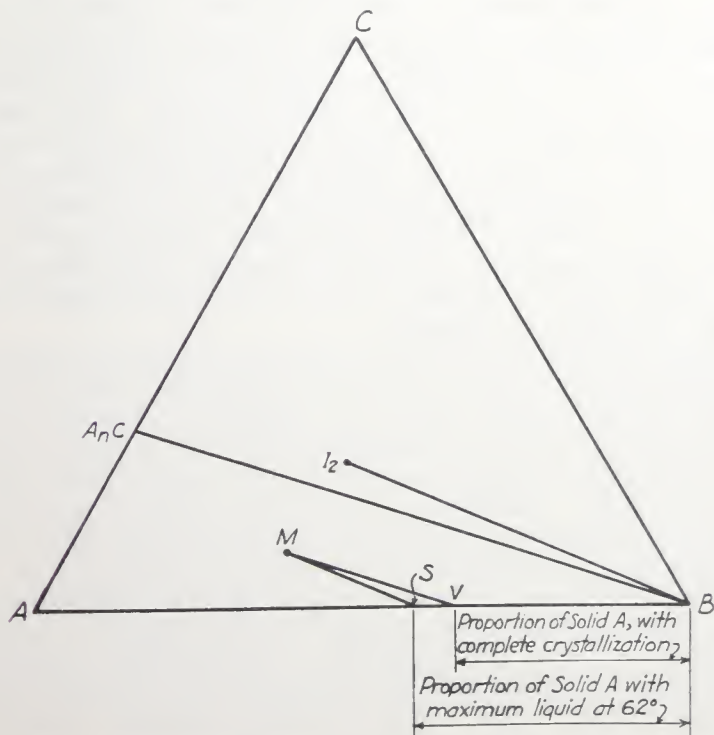


FIG. 12. Diagram illustrating reduction in proportion of one solid phase with crystallization at invariant point not a eutectic.

the proportion of solid A in these figures have been transferred to figure 12. The line MS in figures 10 and 12 is parallel with the line I_2B . The line MV in figures 11 and 12 is parallel with the line A_nC-B . The location of the invariant point I_2 with reference to the triangle $A-B-A_nC$ determines whether the length of VB will be greater or less than the length of SB , that is, whether the proportion of solid A will increase or decrease as crystallization proceeds at point I_2 . If it were inside the triangle $A-B-A_nC$, that is, if I_2 were a eutectic point, VB would be greater than SB , and solid A would increase in quantity during crystallization at I_2 . Since point I_2 is outside the triangle $A-B-A_nC$, solid A decreases in quantity as composition M completes its crystallization at I_2 . This would be true for any composition in the triangle $A-B-A_nC$. In general, when an invariant point is outside of the triangle which includes all compositions completing their crystallization at that point, in a direction away from a vertex X , the solid phase X is present in greater quantity when the liquid arrives at the invariant point than when crystallization is completed.

The decrease in solid A during crystallization at an invariant point is not a mere physical transfer of the molecular species A from one phase to another, since the other phases present when crystallization is completed are the pure solid phases B and A_nC . The process of crystallization is not a purely physical process but involves chemical change.

The rôle of the liquid phase in processes of fusion and crystallization

In dealing with systems in which the number of primary-phase regions is not greater than the number of components, as in figure 1, the processes of fusion and crystallization may be treated as purely physical processes. When there are more primary-phase regions than the number of components, and the invariant points are eutectics, as in figure 6, the course of crystallization, starting with the liquid state, may be treated as a physical process. However, in considering the process of fusion, complete or partial, the chemical changes occurring in the liquid phase must be recognized. In the case of systems in which there are non-eutectic invariant points, as in figure 9, the fact that chemical changes occur in the course of crystallization is apparent.

In processes involving partial fusion of refractory materials the chemical reactions which produce the mineral constituents in the product occur in the liquid phase. For example, portland cement raw mixtures are converted into the cement minerals very slowly at temperatures below that of liquid formation. When the temperature is raised to a point at which liquid appears, chemical changes occur rapidly. The liquid not only acts as a medium of rapid exchange for the various components, but its equilibrium relations with the various possible solid phases in the system determine the solid phases which will be formed.

Descriptions of the course of crystallization in reports of investigations of phase equilibria usually assume an ideal condition in which cooling is so slow that equilibrium is attained at each temperature. Crystallization is treated as a physical process, with departures from this treatment only when the necessity arises because chemical change is evident, and cannot be ignored. This mode of

treatment is proper, since it is impossible to predict all of the possible applications of the phase equilibria data, and the conditions under which departures from the ideal conditions may become important. On the other hand, application of the phase diagram to industrial problems may require consideration of the manner in which equilibrium is attained in the process of fusion, and also the effects of failure to attain equilibrium during fusion or crystallization. In such applications the rôle of the liquid phase must be taken into account.





